Arenes and Aromaticity

28 May 18:31

Is compound Aromatic ?

Huckle Rule

Important Mechanisms :

Nitration
Halogenation
Sulphonation
Friedal craft alkylation
Acylation

Important topics :

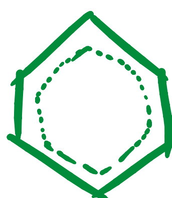
Activating and deactivating substituents and their orientation.

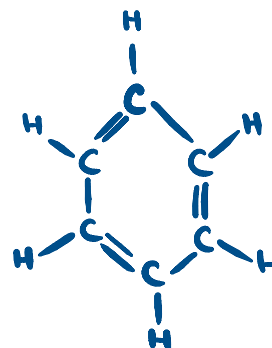
Ortho-para directing groups.

Side chain reaction of benzene derivatives.

Structure of Benzene





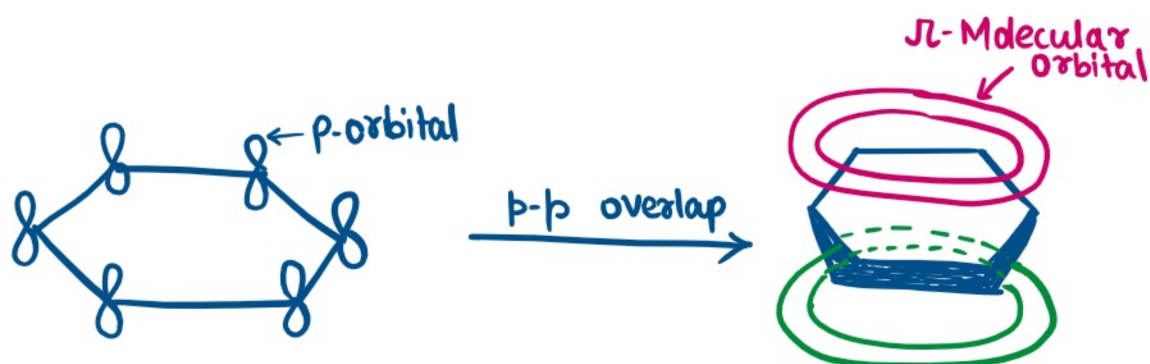


Benzene or Annulene   (short hand representation)   (Expanded form)

Huckel Rule (Aromaticity)

Rule ① : An Aromatic compound must be cyclic and planar (sp^2).

Rule ② : Each atom in an aromatic ring has a p-orbital.
These p-orbitals must be parallel so that continuous overlap is possible around the ring.



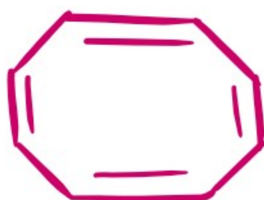
Rule ③ : The cyclic pie Molecular orbital (electron cloud) formed by overlap of p-orbital must contain $(4n+2)\pi$ electron, where $n = 0, 1, 2, 3 \ldots$
This is known as Huckel Rule.

n →	1	2	3	4	5	6	0
πe^- →	6	10	14	18	22	26	2

Examples:

If any sp^3 orbital present, it is Non-Aromatic.

Compound.		← sp^3
cyclic	✓	✓
All sp^2 i.e planar	✓	X
p orbital	✓	✓
Parallel p-orbital	✓	X
$(4n+2)\pi\ e^-$	6 ✓	6 ✓
Aromatic	✓	X



$8\pi e^- \longrightarrow$ Non-aromatic

$(4n+2)\pi = 8$

$4n = 6$

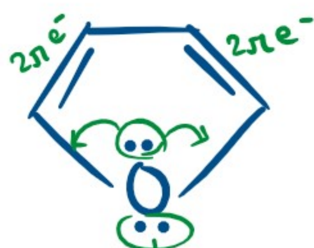
$n = \frac{6}{4} \neq 0, 1, 2, 3, 4 \ldots$

lone pair is also 2 pie electron due to participating in resonance.



$6\pi e^- \rightarrow$ Aromatic

One pair of lone pair is 2 pie electron due to participating in resonance and another pair may not participate in resonance, thus not a part of 2 pie electron.



Donot participate in resonance

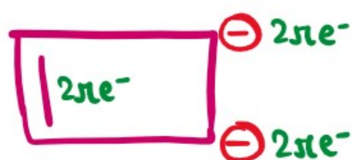
$6\pi e^- \rightarrow$ Aromatic

lone pair directly bonded to double bond donot resonate.



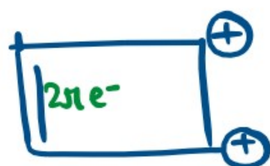
$6\pi e^- \rightarrow$ Aromatic

Negative charge count in 2π electron



$= 6\pi e^- \rightarrow$ Aromatic

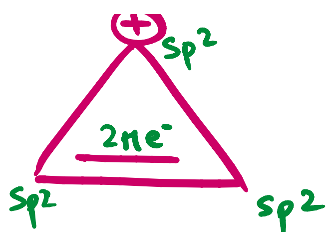
Positive charge not count in 2π electron.



$2\pi e^- \rightarrow$ Aromatic



Not Aromatic



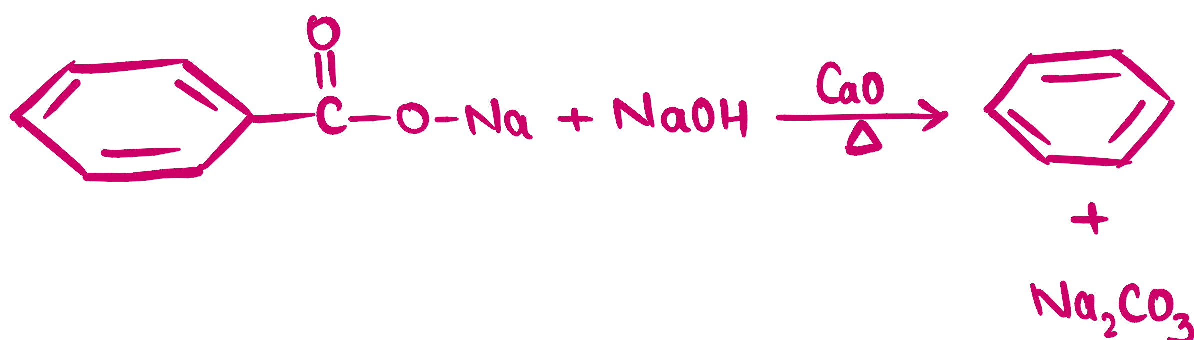
$2\pi e^- \rightarrow$ Aromatic

Small scale Preparation of Benzene

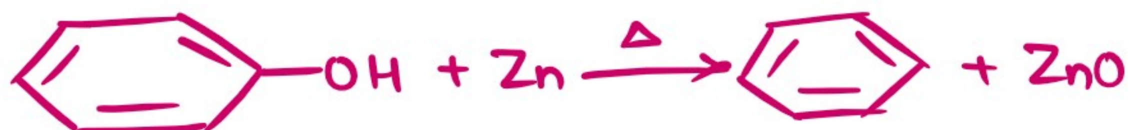
① By passing Acetylene through red-hot tube at 500 degree celcius.



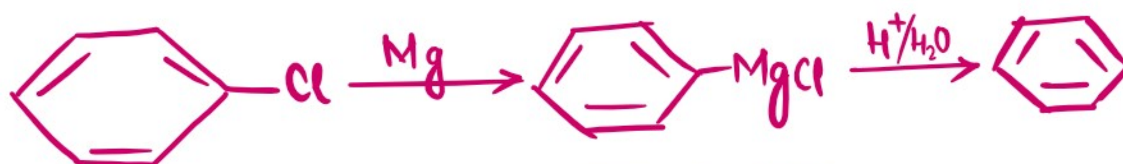
② By heating benzoic Acid or its sodium salt with soda-lime (NaOH + CaO)



③ By heating phenol with Zinc dust

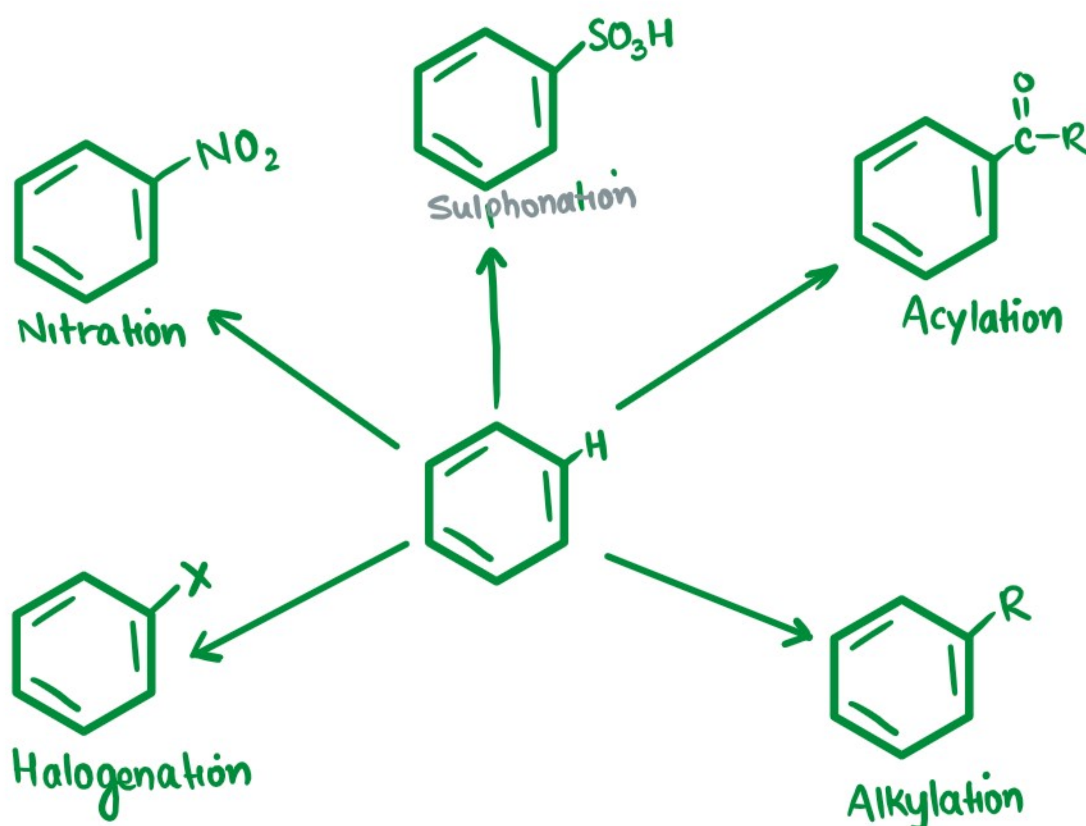


④ By treating chlorobenzene with Mg followed by treatment with dil HCl



Grignard Reagent

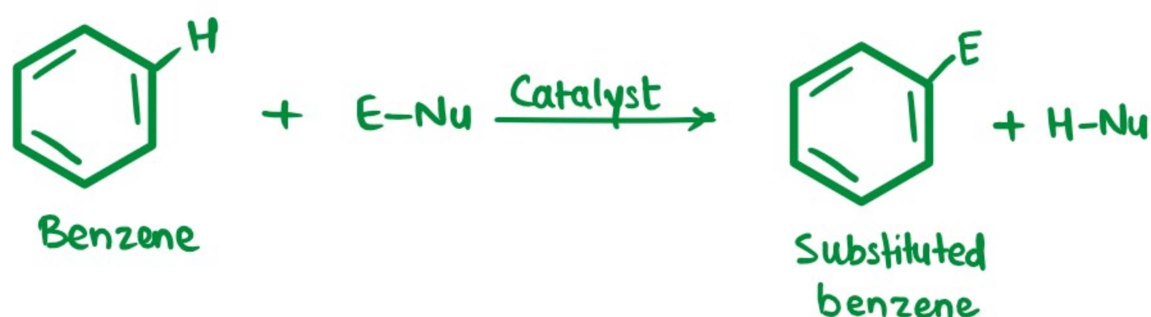
Chemical Reaction of benzene



General Reactions of benzene

- Electrophilic substitution Reaction.
- Addition Reaction.
- Oxidation Reaction.

① Electrophilic Substitution Reaction

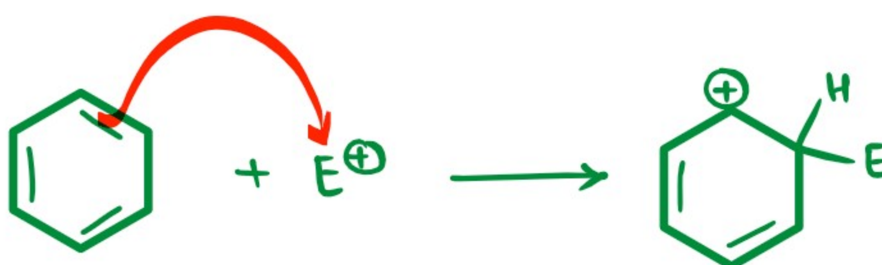


General Mechanism

Step ①: formation of Electrophile



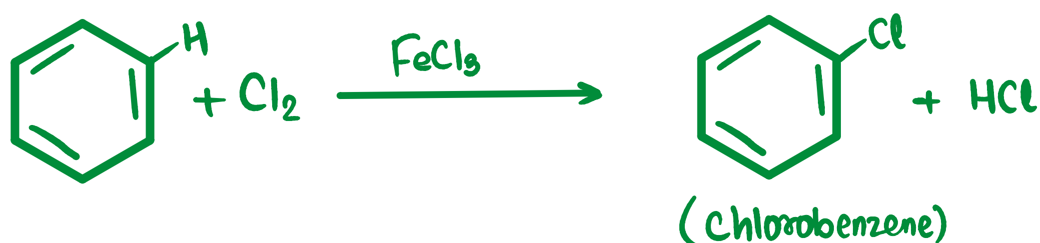
Step ②: The electrophile attack the aromatic ring to form a carbonium ion.



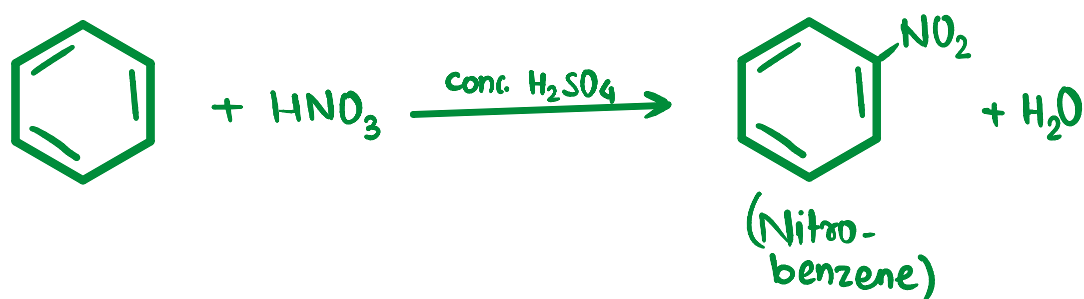
Benzene (Carbonium ion)

Step ③ : loss of proton to give the substitution product.

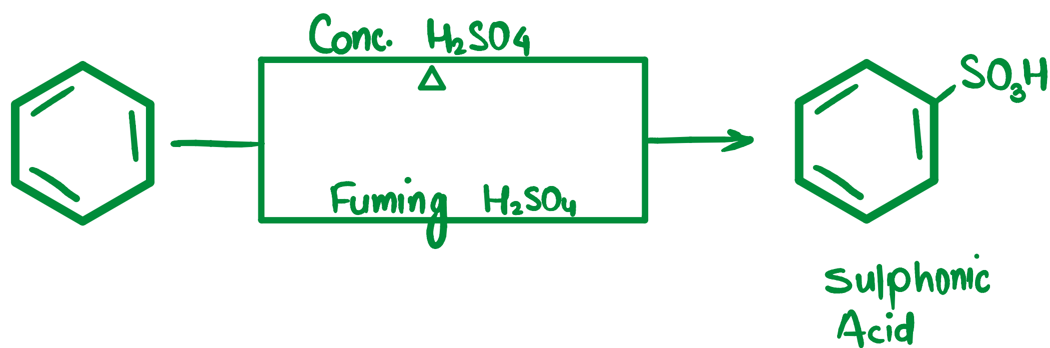
Halogenation



Nitration



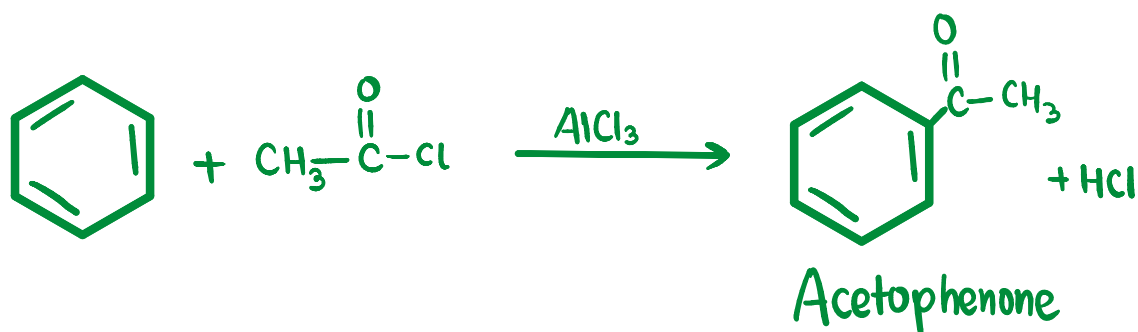
Sulphonation



Friedel - Craft Alkylation

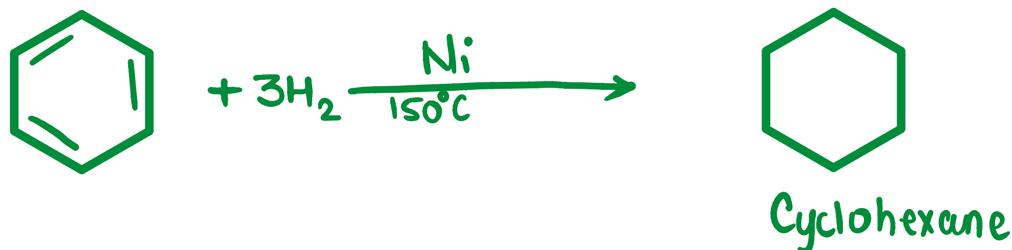


Acylation

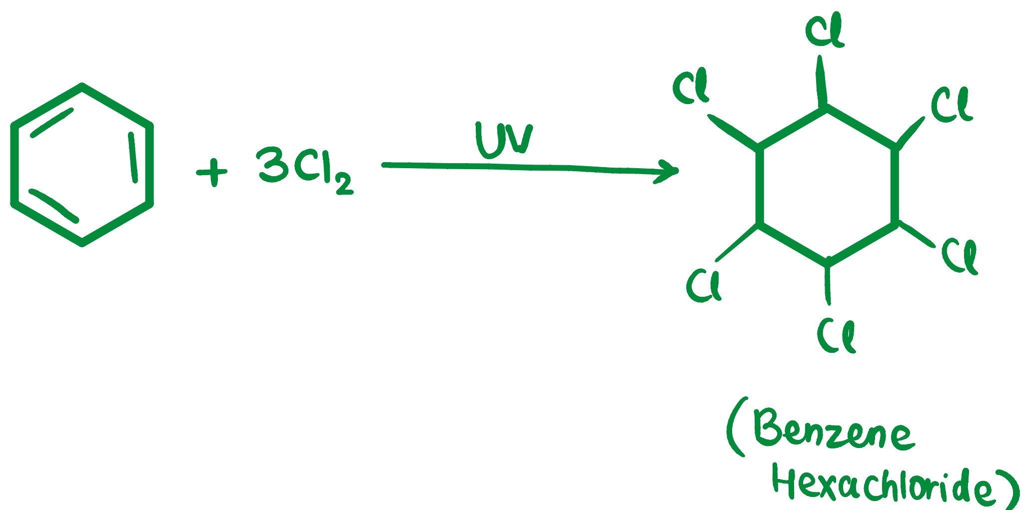


② Addition Reaction

Addition of Hydrogen

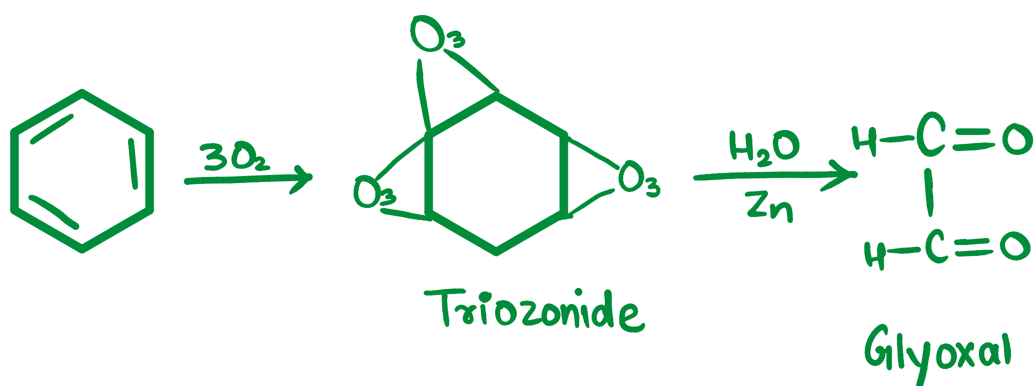


Addition of Halogen



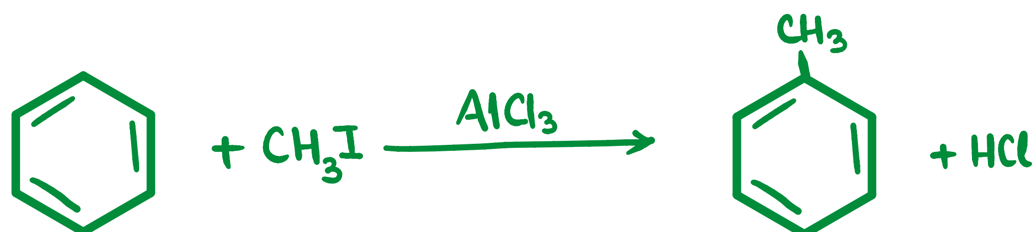
③ Oxidation Reaction

Ozonolysis

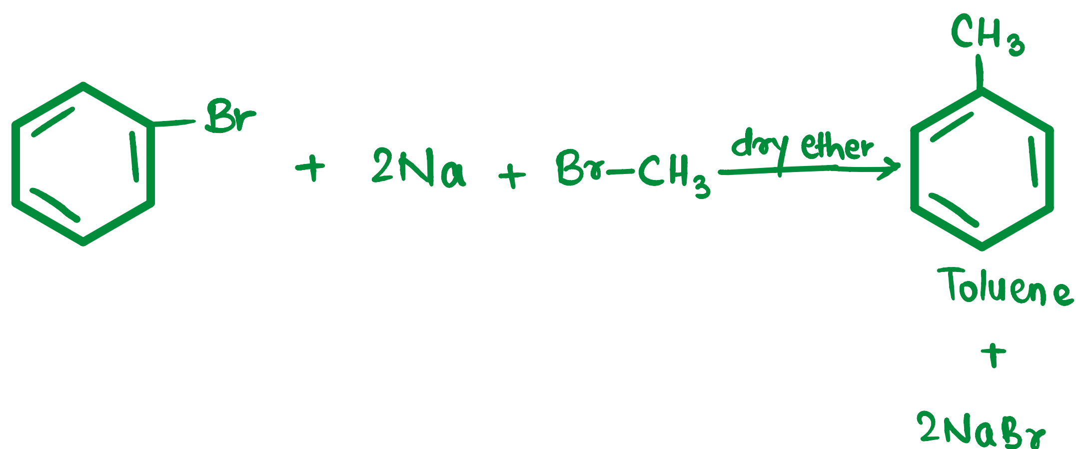


Preparation of Toluene

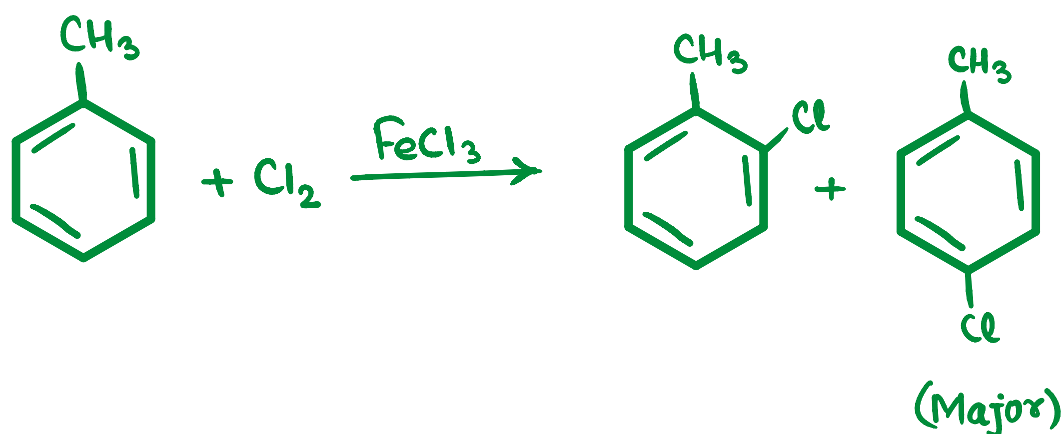
① By Free Radical Alcylation



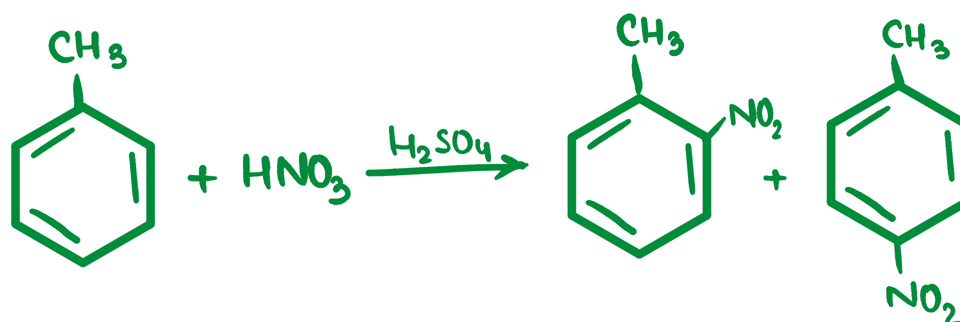
② From bromobenzene by Wurtz-fitting Reaction



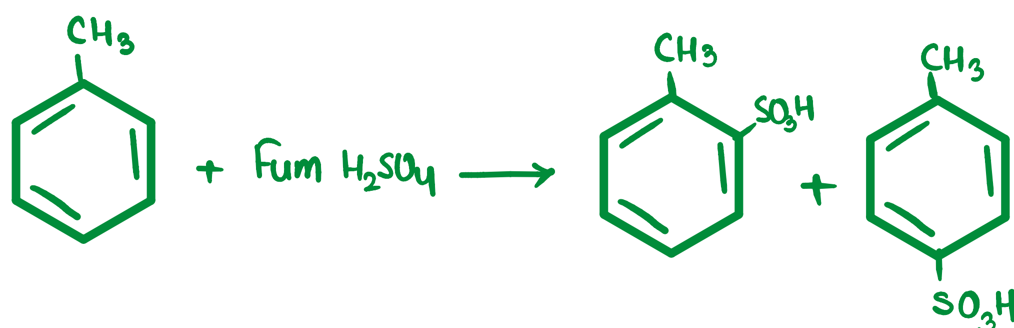
Halogenation of Toluene



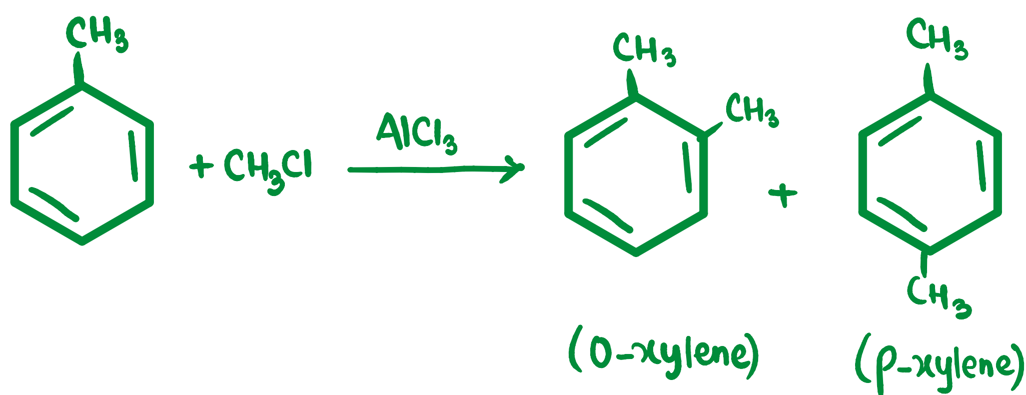
Nitration of Toluene



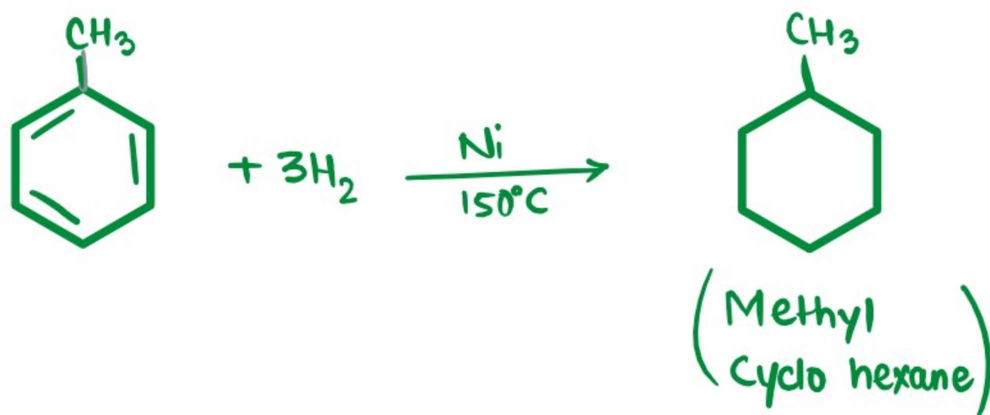
Sulphonation of Toluene



F.C. Alkylation

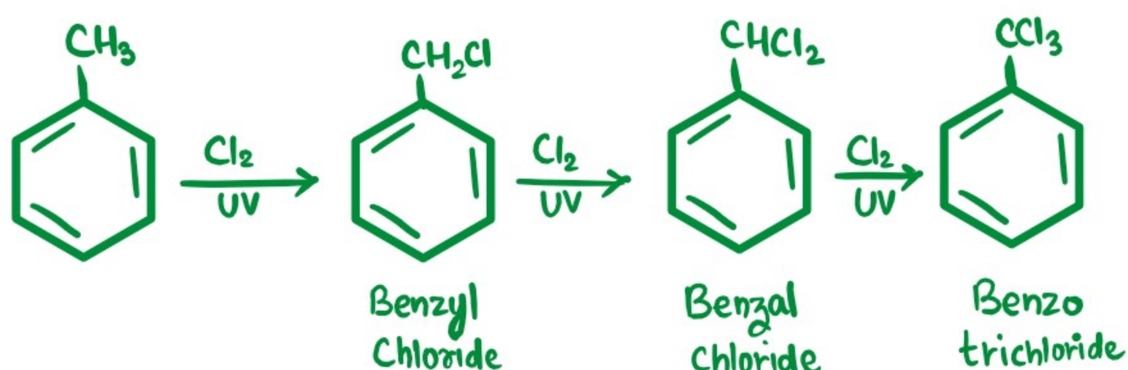


Catalytic Hydrogenation



Side- Chain Reaction

Side chain Halogenation



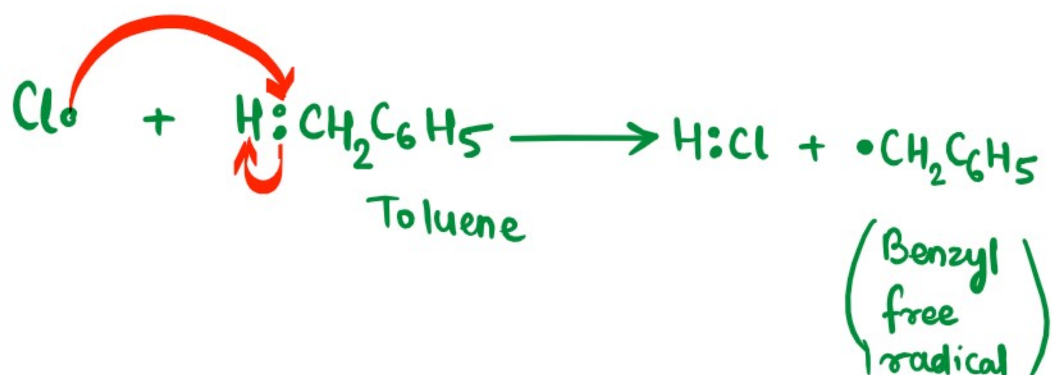
Mechanism

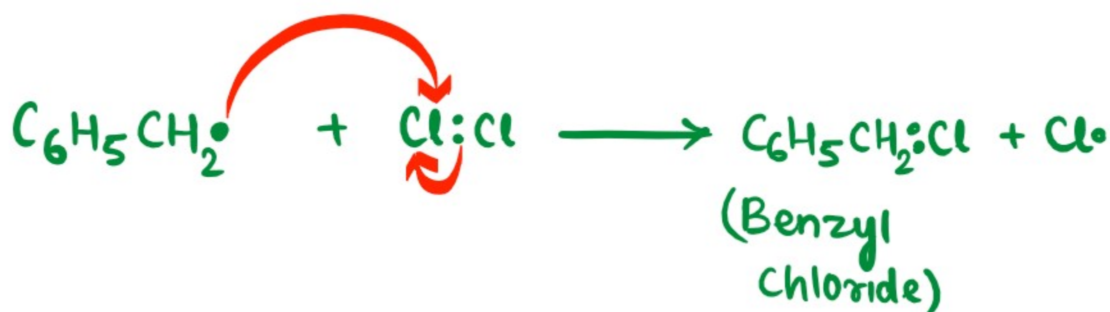
Free Radical substitution.

step ① Chain- Initiation step



step ② Chain propagation step





Step ③ : Chain Termination step



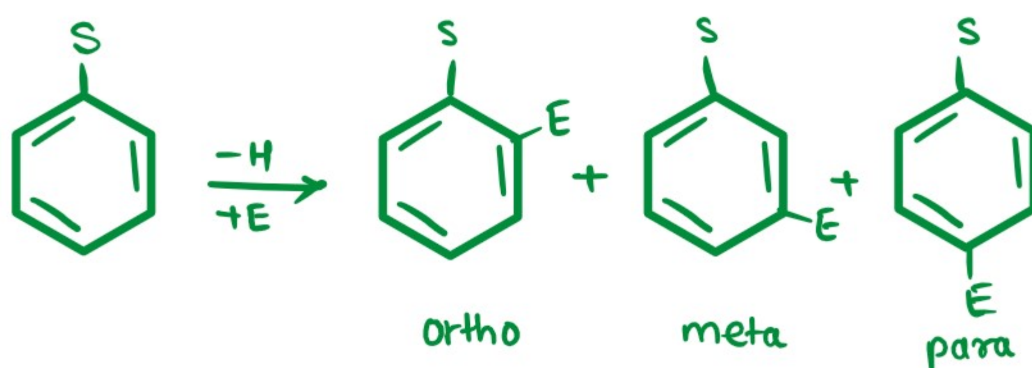




Similarly benzal and benzo formed.

Effects:

Ortho-para directing effect, Meta directing effect, and Activator & Deactivator



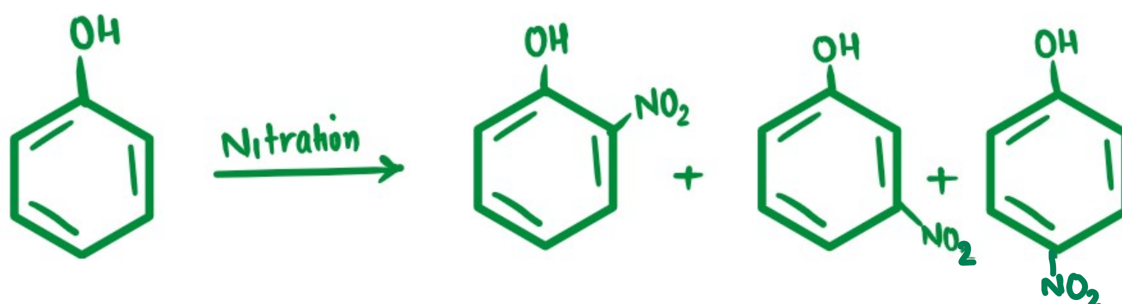
Ortho-para directing groups

$-Cl$, $-Br$, $-I$, $-OH$, $-NH_2$,

$-CH_3$, $-C_2H_5$, $-F$, $-O-CH_3$,

$-OR$, $-R$, $-NR$, $-NH$

$-NHR$

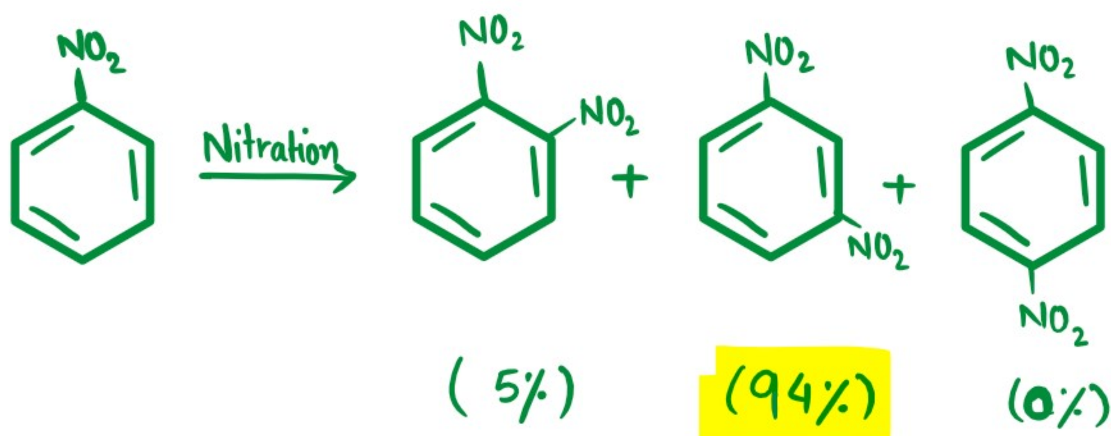


o	m	p
(53%)	(47%)	(0%)

Meta directing group

$-NO_2$, $-SO_3H$, $-CN$, $-COOH$,

$-CHO$, $-CO-R$ (ketone) , $-\overset{+}{N}H_3$ (Ammonium ion)



(5%) (94%) (0%)

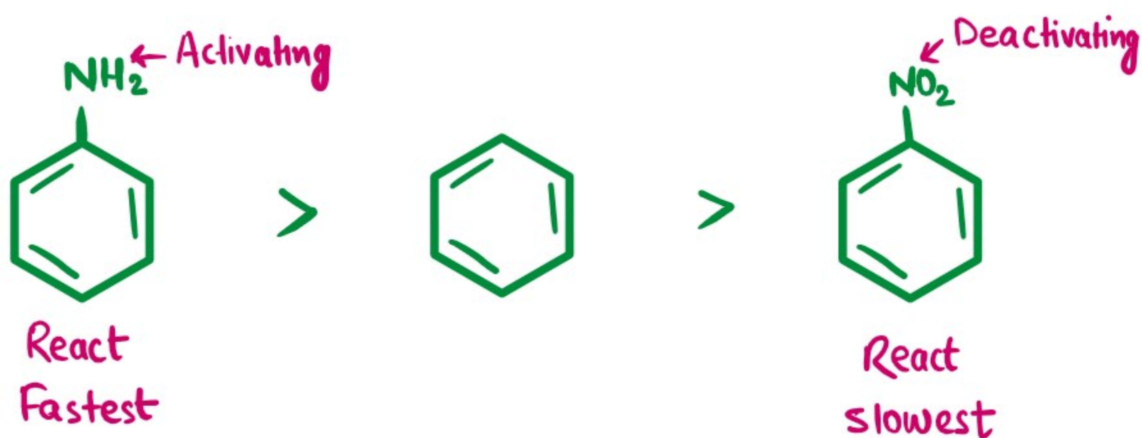
Activating Substituent

A substituent which activates the aromatic ring to further substitution.

Deactivating Substituent

A substituent which deactivates the aromatic ring to further substitution.

Substituent	Effect on Reactivity
O-p directing $-OH$, $-OR$ $-NH_2$, $-NHR$, $-NR_2$	strongly activating
$-CH_3$, $-C_2H_5$, $-R$	weakly Activating
Halogens	Deactivating groups.
Meta directing $-NO_2$, $-CHO$, $-COR$, $-SO_3H$, $-CN$, $-COOH$	strongly deactivating



Important point

Ortho- para directors activates a ring towards Electrophilic Substitution Reaction (E.S.R) whereas meta directing groups deactivates a ring towards E.S.R

-F, -Cl, -Br, -I are ortho-para directors, these deactivates an aromatic ring in E.S.R